

Characterization of the Chemical and Associated Optical Properties of CDOM: Transformations in Fresh to Marine Transition Zones

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LONG-TERM GOALS

The long-term primary scientific objective of our research for ONR is to develop an understanding of the physical and chemical processes affecting chromophoric dissolved organic material (CDOM) and the resultant attenuation changes of ultraviolet and visible radiation in seawater. In the open ocean, optical properties are relatively stable in comparison to coastal environments where complex variations of sources, sinks, and modification processes can result in dynamic and heterogeneous changes to the optical characteristics (attenuation, color, fluorescence) of the surface ocean. CDOM exhibits unusual optical properties, such as an absorption spectrum that is characterized by a featureless exponential increase with decreasing wavelength that makes differentiating between sources (soil, riverine, oceanic) difficult. Our inability to understand these properties results from the limited structural information available on CDOM at the molecular level. Progress on the characterization of CDOM in seawater has been limited by the inability of available techniques to deal with the complex nature of this material. To address these issues, it is necessary to develop unambiguous separation or extraction methods and then to examine the relationship between the optical properties and the structural features of CDOM.

OBJECTIVES

Our long-term objectives are to:

- develop an understanding of the photochemical processes affecting CDOM and the resultant changes in optical properties
- examine the differences and similarities between CDOM of marine vs. terrestrial origin, and the impact these properties have on the chemical and optical characteristics of coastal environments
- characterize the differences between CDOM from different coastal sources and how it varies seasonally (or relative to other parameters controlling its input)
- apply this new knowledge about CDOM characterization to the development of new autonomous real-time remote sensing capabilities that can be applied to global observation

APPROACH

Our experimental approach couples optical characterization of fractionated CDOM by absorbance and fluorescence techniques with structural characterization by LC/MSⁿ. In previous ONR funded studies

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we have used a diffusion-based technique, flow field flow fractionation (FIFFF), to examine the relationship between molecular size distribution and optical properties, while independently analyzing the samples by direct infusion into an LC/MSⁿ system. This year Mr. Erik Stabenau (graduate student) developed an alternate inline diffusional analysis for the LC/MS system based on gel filtration chromatography with UV, fluorescence and ESI-MSⁿ (Bruker Daltonics, Inc.) detectors in series.

WORK COMPLETED

FIFFF:

Flow field-flow fractionation (FIFFF) coupled with absorbance and fluorescence detectors was used to separate the CDOM molecules based on their diffusion coefficient (D), spectroscopy which is a function of molecular size, and to characterize the different fractions based on their optical properties. Dr. Eliete Zanardi-Lomardo completed her dissertation research, applying FIFFF to examine several southwestern Florida freshwater inputs to the coastal waters, and graduated in December 2002.

LC/MS:

Methods were developed and refined for using this instrumentation to study natural samples. The system produces a large volume of data, which was difficult to visualize or evaluate in a meaningful quantitative or qualitative manner. Data routines were developed to elucidate the general characteristics of the sample, describe them in mathematical terms and relate them to their optical properties. Gel filtration chromatography methods were developed for LC/MSⁿ to examine the relationship between diffusional properties, molecular mass and optical properties of fresh to salt water samples. Mr. Erik Stabenau has completed a major draft of his dissertation "Photochemistry and Structure of Environmental Macromolecules" and expects to graduate in December 2003.

RESULTS

Figure 1 shows the chromatographic trace of the absorption coefficient for two of the seven stations sampled in the Shark River slough revealing three regions of significant absorption for station 8 and only two regions for station 3. The variation in retention time for these three peaks are plotted against salinity in Figure 5.9, showing that all three conditions, increasing, decreasing, or relatively constant molecular weight were observed for these three peaks. Peak 1 has the highest molecular weight and was not observed at the lowest salinity station in the river but appeared with increasing concentration and decreasing molecular mass along the river transect toward more saline waters. Peak 2 had an intermediate molecular mass that increased slightly during water transit toward more saline waters. Peak 3 had a relatively stable and low diffusion based molecular mass throughout the river system. Total absorbance increased in the mid-river stations and then decreased as waters transferred from low salinity inland conditions toward the coast, perhaps indicating an in-water source of chromophoric material.

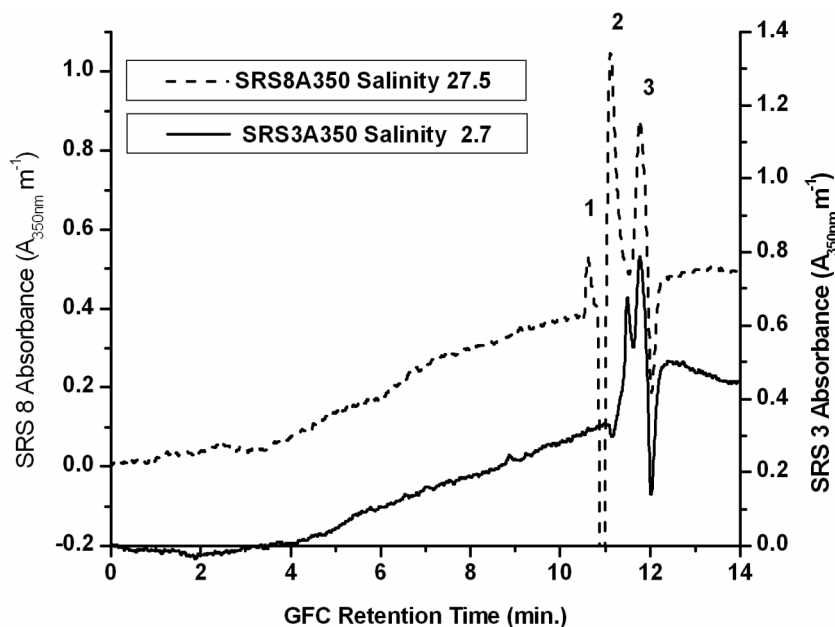


Figure 1 Gel Filtration Chromatography based chromatogram showing UV absorbance vs. retention time for Shark River slough Station 8, Salinity 27.54 (dashed) and Station 3, Salinity 2.71 (solid). Plot reveals decreases in peak retention time, indicating an increase in mass, and variation in the abundance and number of peaks for samples collected at different stations within a single river. Note offset in y-axis used to allow clear viewing of each trace.

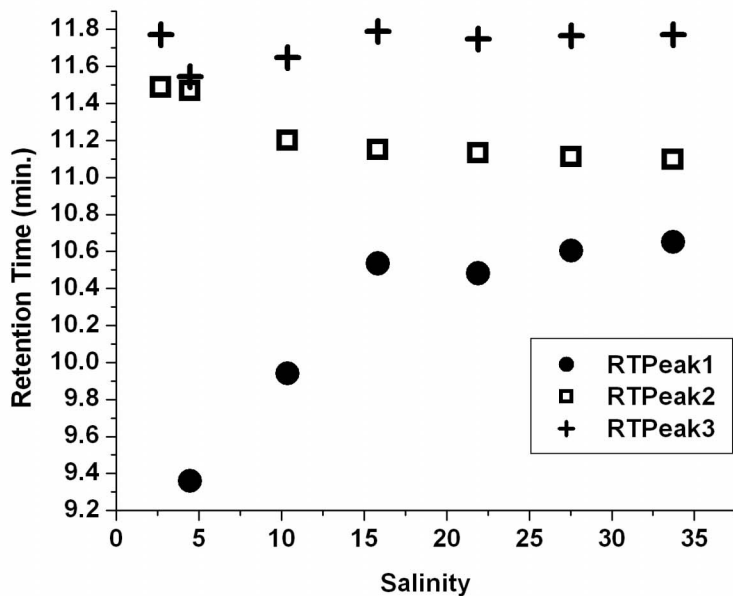


Figure 2: Graphs shows the variations in retention time vs. salinity for the three peaks identified in figure 1 at each sample location in the Shark River. Peaks show either an increase in retention time that is interpreted as an increase in molecular mass, a decrease in retention time that is interpreted as a decrease in molecular mass or constant retention time indicative of constant molecular mass as a parcel of water is transferred down the river. All data is based on the diffusional properties of compounds absorbing at 350 nm.

In comparison, the molecular mass as directly measured by ESI-MS did not correspond to the diffusional mass derived from retention time. Peak 1, for instance, had a diffusional mass in excess of 100 kDa however the associated mass spectra revealed a series of masses starting at 260 Da with $\Delta m/z$ of 142. Since the compounds found at this retention time are optically active, it appears that, although the diffusional size of the compound is much larger, the chromophore itself may be a relatively small unit of no more than 142 Da. If this is not the case then either the chromophore is not ionizing and being delivered to the ion trap or the chromophore is created by extended conjugation between these small sub-units.

It is of interest that the mass distribution observed for these experiments based on their diffusional properties is quite different than measured by mass spectrometry. The simplest explanation of the difference in diffusional versus directly measured mass is that the diffusional mass observed is from a large complex, based on a weak interaction between subunits, which are easily disrupted during the electrospray ionization process. Alternatively, there may be compound specific interactions between the chromophore containing moieties of CDOM and the gel filtration column that alter the behavior of the target compounds relative to the polymeric standards used for calibration. Neither of these theories could be confirmed with the current data. One limitation of this technique has been low recovery of CDOM from the gel filtration column. The specific mechanism of the non-reversible absorption of chromophoric compounds onto the gel material needs further investigation.

IMPACT/APPLICATIONS

Predictive models of ocean color incorporate CDOM through the use of the apparent absorption coefficient. This is a cumulative property developed from mixed CDOM with mixed wavelength dependent features that have proven difficult to predict in dynamic coastal environments. The previous years work has been focussed on developing enough structural information to determine the specific absorption coefficient for the chromophoric moiety(ies). The specific absorption coefficient has a rigorous relationship between structure and photochemical activity, which should improve modelers' ability to predict the spectral dependence of light absorption. Additionally, a rigorous and predictive model of light absorption is critical for the interpretation of satellite signals, including understanding the depth of penetration of specific wavelengths of light and the depth dependent partitioning of solar energy in surface waters.

TRANSITIONS

The ESI-MS technique developed in this program is currently being used by the US-EPA to determine similarities between CDOM in coastal zones and that produced during the degradation of submerged aquatic vegetation. In that study a combination of hyperspectral absorbance data and ESI-MS determined mass distributions, developed in the current study, are being used to determine the relative contribution of specific in water sources of CDOM to light attenuation over the continental shelf.

RELATED PROJECTS

Drs. Rod Zika, Paula Coble and Richard Zepp are serving as special editors for an issue of Marine Chemistry which will publish as a group papers arising from the session on CDOM at the 2002 Ocean Sciences meeting in Hawaii.

Dr. Rod Zika is the Chief Scientist for The International SeaKeepers Society, which has developed and deployed an autonomous ocean and weather monitor system on commercial ships, piers, buoys and private yachts as participants in the Volunteer Observing Ships (VOS) program. In partnership with several oceanographic instrument manufacturers, SeaKeepers is developing and field-testing miniaturized optical sensors for chlorophyll-a and CDOM fluorescence, which can be fitted as modules in the SeaKeepers system. Near-real time weather observations are transmitted to the National Weather Service every 3 hours, and high-resolution (1 minute) data is stored on the hard drive for retrieval at intervals and entry into the SeaKeepers database. The database will be available for general use.

PUBLICATIONS

Stabenau, Erik and Rod G. Zika. Correlation of the Absorption Coefficient with a Reduction in Mean Mass for Dissolved Organic Matter in Southwest Florida River Plumes. *Mar. Chem. Special issue on CDOM* [In press, refereed]

Zanardi-Lamardo, Eliete, Cynthia A. Moore and Rod G. Zika. 2004. Seasonal variation in Molecular Mass and Optical Properties of Chromophoric Dissolved Organic Material in Coastal Waters of Southwest Florida. *Mar. Chem. Special issue on CDOM* [In press, refereed]